PERMANENT FILE COPY

MAIN FILE

OTS: 60-41,500

JPRS: 4078

29 September 1960

ACTIVE CENTERS IN AN ACETYLENE FLAME

By Te. Kondratiyeva and V. Kondratiyev

- USSR -



Approved for Public Release Distribution Unlimited

Distributed by:

OFFICE OF TECHNICAL SERVICES U. S. DEPARTMENT OF COMMERCE WASHINGTON 25, D.C.

Reproduced From Best Available Copy

· Carried Barrier

U.S. JOINT PUBLICATIONS RESEARCH SERVICE 205 EAST 42nd STREET, SUITE 300 NEW YORK 17, N. Y.

DTIC QUALITY INSPECTED 4

20000707 178

JPRS: 4078

CSO: 1054-S

ACTIVE CENTERS IN AN ACETILINE FLAME

-USSA-

[Following is the translation of an article by Ye. Kondrat'yev and V. Kondrat'yev entitled "Aktivnyye tsentry v plameni atsetilena" (English version above) in Zhurnal Fizicheskoy Khimii (Journal of Physical Chemistry), Vol XXI, No 7, Moscow, 1947, pages 761-768.]

The successful application of a catalytic method to the detection and measurement of the concentration of atoms of hydrogen in hydrogen flames (1) has made it possible for one to expect the method to be effective also for measurements of other flames. Of especial interest are the flames of hydrocarbons in view of the extensive theoretical and practical significance which the mechanisms of these reactions hold. For this reason every new experimental method here is especially valuable.

Experimental Procedures

In order to avoid the high temperatures which are characteristic of acetylene flames, we studied acetylene-air flames, as before, under pressures of several millimeters of mercury (the jet method). The same reaction vessel and the same thermocouple were used as in our previous experiments with hydrogen flames. As a catalyst, we used ZnO·Cr₂O₃. The acetylene was obtained by the action of water on powdered calcium carbide and after probul'kivanie /? / through solutions of potassium dichromate, sodium hydroxide, and copper nitrate, it was collected in a gasometer with a saturated aqueous solution of sodium chloride. Before entering the reaction vessel the acetylene was dried out with phosphoric an-

hydride. The air was contained in a separate gasometer and was also dried (sulfuric acid and phosphoric anhydride). Dry acetylene and air were supplied through a valve which regulated their rate of feed and hence the composition of the reaction mixture and the pressure in the reaction vessel, and entered into the mixer and further into the reaction vessel. From the latter the gas was evacuated by an oil pump, which gas then passed through the volume of a trap cooled by liquid air in which were condensed the remaining unconsumed acetylene, carbon dioxide, water, and other condensable products of the reaction.

The gas pressure in the reaction vessel was measured by a menometer filled with paraffin oil; upon conversion into millimeters of a mercury column the indicated manometer yielded a figure of 15.5 (equal to the ratio of the density of mercury to oil). The temperature in the interior of the reaction vessel was measured with the aid of the two thermocouples (controlling), which consisted of a thermo-electric probe. The end of the second thermocouple was plated for a length of five millimeters with 2nO·Cr_{O2}. The experiments were conducted at pressures in 2the interval of 4.8-10.6 mm of Hg, at temperatures of 650-800°C (maximum temperatures which correspond to the center of the reaction zone), and with compositions of acetylene-air mixtures corresponding to values of the quantity

 $\alpha = \frac{10_2}{3.5(C_2H_2)}$

((0₂) and (C₂E₂) are the volumes of oxygen and acetylene entering each second into the reaction vessel) from 0.36 (rich mixtures) to 6.54 (poor mixtures).

We observed the maximum initial heating, which was measured at a variety of temperatures by the catalytic and control thermocouple, namely the quantity AT, which comprised several tens of degrees. First of all it had to be satisfied that these initial heatings were dependent on the recombining active centers and not on the heterogeneous reaction arising on the surface of the catalyst. The recombining character of the initial heating is clearly seen in the damping action of the probe, which includes a considerable lessening of the brightness of the flame upon the introduction of the probe into the combustion zone and which is related to the retardation of the reaction apparently as a consequence of the drawling off of the active centers, which were adsorbed

(recombining) on the surface of the catalyst. gous retardation action of the probe has been established by us also for hydrogen flames, where the decrease in the percentages of combustion related to the retardation of the reaction can be detected in an increase in the pressure in the reaction vessel (3). The combustion of acetylene in air under the conditions of our experiment proceeded practically without change in pressure. - this reason, here the retardation of the reaction can be judged either from the continual changes of the percentage of combustion or from the diminishing of the brightness. A parallel course in the diminishing of the brightness and the decrease in the initial heating, which is analogous to the slope (khod) of Ap and AT in the case of a hydrogen flame (figure 2 (3)), appears from the following table where there are gathered the values of AT and the flame brightnesses (qualitatively), which were observed upon the positioning of the probe for various distances (?) from the end of the burning portion of the reaction vessel:

> cm . . . 0 2 3 4 5 6 7 8 10 T . . . 0 4 9 12 12 8 3 7 2

flame brightness . br. br.br.bnav. pr.v.pr.av.br.

 $(p = 5.87 \text{ mm Hg}; C = 2.02; t_{max}^{o} = 733^{\circ}C)$

Abbreviations: br. - bright; av. - average; pr.-poor; v. pr. - very poor

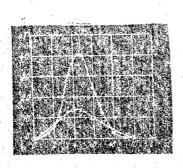


Figure 1

As is seen from this table the minimum A T coincides with the minimum flame brightness, from which follows a direct relationship between the amount of initial heating and the rate of combustion.

The damping action of the probe arises in the case of the richer mixtures: at $\alpha < 1$ the flame may be completely absorbed upon the introduction of the probe. Furthermore, as also in the case of the hydrogen flame the

probe action is the more noticeable the lower the pressure and temperature (especially the pressure). At large enough pressures the curve AT: / has a smooth slope. Such curves, in particular, are displayed in figure 1, where the lower one is obtained at p = 7.48 mm, to = 688° C, and A = 4.05, the upper curve at p = 8.74 mm, to = 729° C, and A = 2.14. We add that in these also max analogous cases the flame brightness is practically independent of the position of the probe (?). For this reason it may be assumed that the introduction of the probe in the combustion zone substantially does not affect the coheentration of the active centers in the flame (this effect is bounded by a quite moderate volume, which continually surrounds the catalyst) and the observed initial heating AT closely corresponds to their actual concentration.

Another, even more convincing, demonstration of the recombining character of the initial heating lies in the fact we established that the measured initial heating is observed solely in the presence of the flame. In particular, this is seen from the data of table 1, in which it appears that in spite of the closeness of the temperatures of the catalytic thermocouple (t), the initial heating AT = t - t (t is the temperature of the control thermocouple) is the absence of the flame (K<1) is equal to zero. In this regard especially demonstrative is a comparison of experiments Nos 65 and 87, as here the initial partial pressures of acetylene and oxygen in the burning gas (No 87) is less than the corresponding pressures of the unburned gas (No 65); a significant initial heating is not less in the first case, but in the second case it is equal to zero.

From the foregoing it is clear that the initial heating in the acetylene flame which we have observed, at least under the conditions of our experiment (relatively low temperatures and pressures), is dependent practically solely on the recombining active centers on the sur-

The following, significantly more difficult, questions are questions on the nature of these active centers. Spectroscopic investigation of the acetylene-air flame has indicated the presence in the flame of the radicals OH, CH, C2 and HCO. According to the computations by Avramenko (2) based on the measurements of the absorption spectrum of hydroxyl, the average concentration of this radical in the flame corresponds to the pressure of an order of magnitude of several hundred fractions of a millimeter of a column of mercury (at a pressure of the order of several tens of millimeters). As concerning the concentration of the radical CH, our computations from I

the relative intensities of luminosity of CH and CH (4) at a set normally likely luminosity of CH (of the order of 10° sec -1) leads to the ratio $p_{OH}: p_{CH} \geq 1000$. At a still lower concentration (4>1) is the radical C_2 . Further, the low intensity of the luminosity band of HCO sllows one to state that the concentration of this radical in the flame may also be taken as a insignificant amount.

Along with the radicals which were detected in continuous spectroscopy, in the acetylene flame there needs be assumed also the presence of other active centers, which is likely on the basis of one or another indirect considerations. Thus, in the reaction of hydroxyl and other active centers with a molecule of acetylene there needs to be related the appearance of the CoH radical. Further, as a result of the reaction of hydroxyl with carbon dioxide, which is found in the acetylene flame at a considerable concentration, there are formed atoms of hydrogen. It is possible that the foregoing is accounted for also as a result of the hypothetical reaction C2H + 02 = C0 + HC0 -> 2C0 + H. In the conditions of the flame atoms of hydrogen undoubtedly yield atoms of exygen (the reaction $H + O_2 = OH + O$) whose appearance may be related to the reaction CH + O2 = HCO + O. The probability is not excluded of the presence of still other active centers in the flame (for example, the radical CH2). 4

Concerning the concentrations of the active centers mentioned, they may be computed only very approximately. Thus, allowing the invariance (statsicharnost') of the redical C2H and the related disappearance of it in reaction with oxygen, we can set down the conditions

of the invariance in the form of:

 $\sum k_i p_i p_{C_2 H_2} = k p_{C_2 H_2 O_2}$,

where p, is the partial pressure of the i-th active center of the free atom type (H, O) or a radical (OH and others); PC2H2, PO2, are the partial pressures of acetylene, 2H2, PO2, are the partial pressures of acetylene, 2H2, and k are the constants in the rates of the corresponding reactions. In view of the fact that the constant may scarcely make a contribution more than the constant k, we must conclude on the basis of the foregoing equation that at near PC2H2 and PO2 the concentration of the radical C2H must be 2H2 of an 2 order of magnitude not less than the concentration of the most abundant active center, such as, it appears, is atomic hydrogen

(cf below).

We can evaluate the concentration of the atoms of hydrogen and oxygen in the acetylene flame starting from the known concentration of hydroxyl, which is undoubtedly invariant (stationarmaya), as also the concentration of H and O (5). Helating the appearance of hydroxyl in a reaction with these atoms to that corresponding to oxygen and acetylene, and the disappearance of hydroxyl, is its reaction with acetylene; and so, from the condition $\theta_{eM} = 0$, we will have

from the condition
$$\frac{Q_{eW}}{dt} = 0$$
, we will have $k_{\rm H} p_{\rm O_2} p_{\rm H} + k_{\rm O} p_{\rm C_2H_2} p_{\rm O} = k_{\rm OH} p_{\rm C_2H_2} p_{\rm OH}$

Precisely so is the relating of the formation of atoms of oxygen in the reaction of H with O2, and the disappearance is the reaction of O with C2H2; from the condition # O2 = O, we will obtain

and, consequently,

$$p_{H}: p_{OH}: p_{O} = \frac{k_{OH}}{2k_{H}} \cdot \frac{p_{O > H_{2}}}{p_{O}} : 1 : \frac{k_{OH}}{2k_{O}}$$
, or, setting $p_{O_{2}}$

Of the constants arising in this ratio, only the constant k, is known, for which Voevodskiy (6) has given the following formula:

$$k_{\rm H} = 6.4 \cdot 10^{-12} \sqrt{\rm T} \cdot {\rm e}^{-\frac{18000}{\rm RT}} \, {\rm cm}^3/{\rm sec}.$$

Setting approximately $k_0 = k_{0H} = k_1$, where k_1 is the constant of the reaction $OHO + H_2 = H_2OH = H_2OH + H_3$, where k_1 is the constant of the reaction $OHO + H_2 = H_2OH = H_3$.

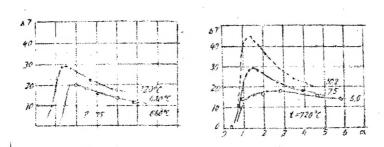
$$k_1 = 7 \cdot 10^{-12} \sqrt{2} \cdot e^{-100} \cdot cm^3/sec$$

and assuming $\alpha = 2$, we will obtain for T = 1000° K

In such a way, according to our approximate evaluation the concentration of atomic hydrogen in the acetylene flame must be of an order of magnitude greater then the concentration of the hydroxyl; the concentration of atomic oxygen must be one order of magnitude near the hydroxyl concentration. As has been already shown above, the average concentration of hydroxyl in the acetylene-air flame, at a pressure of some tens of millimeters of a column of mercury corresponds to a partial pressure of the order of a hundredth of a millimeter. Hence, at these conditions the partial pressure of atomic hydrogen must be of the order of a tenth, and of atomic oxygen -- the order of a hundredth of a millimeter. According to the foregoing, the partial pressure of the radical CoH must be not less than a tenth of a millimeter. We add that the partial pressure of the radical CHo is likely not to exceed the partial pressure of the radical CH.

Now then, as a result of the approximate computation of the concentrations of the various radicals in the acetylene-sir flame we arrive at the conclusion that the largest concentration, exceeding the concentrations of the remaining active centers by ten times and more, must be that of the atomic hydrogen and the radical CoH. Obviously, the question is only concerned with the recombination of these active centers and the related initial heating. Concerning the atomic hydrogen, that, as is known, has a probability of recombining on the ZnO·CroOz close to one. With regard to that of the recombination of the radical CoH, this may be founded upon one or another assumptions, which however are difficult to establish. Thus, it can be assumed that the catalytic recombination of CoH is related to the process 2C2H = C2H2 + C2. There is not excluded the possibility of a catalytic reaction of C2H with Both these reactions require the splitting of the molecule CoH and hence must be attended with a certain activation energy. Therefore, the probability of the recombination (or the reaction) of Con must be markedly less then one, which makes it likely to ascribe a significant share of the recombination thermal effect (if not all the effect) to the atomic hydrogen.

That is the way it must be in the case when the heat balance of the catelytic thermocouple is determined by the flow of gas. If the very basic role in the heat balance is played by the diffusion (as appears to us most probable), then as a consequence the rate of



Figure

Figure.

(Coordinates in Figure 2 are in of for the abscissa and run the same as in Figure 3.)

diffusion of the radical CoH must be one order of magnitude less than the diffusion rate of the atoms of hydrogen, and under similar concentrations for both the initial heating must be dependent mainly on the recombination of atoms of hydrogen.

This conclusion is confirmed by our measurements of the quantity AT (initial heating). The results of these measurements are presented in figures 2, 3 and 4. In figure 2 the measured values T are shown in dependence on the mixture composition (α) at various maximum temperatures (the temperature in the center of the reection vessel) and at a pressure p = 7.5 mm Hg. In figures 3 and 4 the dependence of AT on at various pressures and two constant temperatures to = 720°C (figure 3) and to = 680°C (figure 4). As is seen from these figures, the maximum initial heating which was observed in the center of the reaction zone is expressed in several tens of degrees. Arising from this evidence, that the initial heating AT is dependent on the recombination of the atoms of hydrogen, and taking the conditions of the heat belance of the thermocouples in the acetylene flame to be close to a carbon dioxide flame, in order to determine the order of magnitude of the concentration of atomic hydrogen in acetylene-air flames we employ the formula

$$\frac{P_{H}}{P} = 0.25 \cdot 10^{-4} \text{ T. /See Note.} 7$$

From this formula, at p = 10 mm Hg and A T is of the order of several tens of degrees (cf figures 1-4), we obtain for the partial pressure of atomic hydrogen a quantity of the order of 0.01 mm Hg.

([Note 7 Cf our following article. We note that

in the case of the hydrogen flames we found

$$\frac{P_{\rm H}}{P} = 5 \cdot 10^{-4} \Delta x \ (1).)$$

We will show that a quantity of that same order of magnitude is obtained in the measurements of the concentration of hydroxyl. For figures 4 and 5 see p 10]

Actually, Avramenko (2) obtained the following partial pressures of hydroxyl in an acetylene-air flame of stoichiometric mixture:

Extrapolating these values to p = 10 mm, we will find that p_{OH} is of the order of 0.001 mm, that is, a magnitude one order less than that calculated by us for the partial pressure of atomic hydrogen, which completely agrees with the calculations made earlier by us for the relative concentrations of H and OH.

The known qualitative basis for the correctness of our conclusion lies in the fact that the initial heating. T is basically dependent on the recombination of the atoms of hydrogen, which can be seen also from the following fact. As follows from the foregoing above (page 764) the relation between the partial pressures of atomic hydrogen and hydroxyl in an acetylene is approximately

 $p_{\rm H} \sim p_{\rm OH}$

Therefore, the slope of the quantity $\frac{p_{OH}}{p_{H}}$ with must be similar to the slope of the quantity p_{H} . Plotting the measurements of Ayramenko (2), at various pressures and compositions of the acetylene-air mixture (), for the value of the coefficient of the absorption of hydroxyl μ ?, divided by α (in arbitrary units), which coefficient values are approximately proportional to the average values of p_{OH} : α , we actually obtain curves

Table 1

a/	by week	a	рим	+Calla MM	Po.Mu	toc.	t,°€	ΔT	1:4
c/ 46 d/ 73 c/ 45 d/ 87	ri terb Papiri By poles Papiri	0 64	9,35 8,64	0,95	1,03 1,90 1,52 1,42	713 707 657 658	713 669 657 645	0 33 0	5 3,5 5

Legend: a) Number of experiment: b) Flame: c) Does not burn: d) Does burn: e) Remark: L is the distance from the end of the burning portion of the reaction vessel, at which is measured the values presented for to and to.

Table 2

a) N	et	p. Mitti	2°С1Н2.	^{UC} aHs	200.	24,0	*60	v _{ર્સા}	r %.
94 95	£, g 2,69	112,5	0,130	0,027 0,040	0 050 0 057	0,111	0. 156 0. 133	-0 c08	0,70

Legend: a) Experiment number.

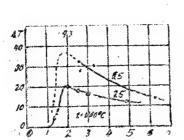


Figure 4

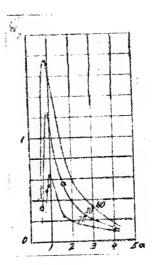


Figure 5

(figure 5), similar to the curves we obtained as shown in figures 3 and 4. A significantly sharper form of the maximum of the curves in figure 5 is undoubtedly ascribable to higher pressures (20, 30 and 40 mm Hg) and temperatures. However, the quantitative comparison of the data in figures 5, 3 and 4 is of no avail, since in the experiments of Ayramenko the temperature of the flame was not measured.

In conclusion we present certain facts relating to the analysis of the products of the combustion of acetylene under the conditions of our experiments (low pressures and temperatures). The weak, and scarcely perceptible odor (at <>1) which is apparent upon the evaporation of the reaction products that are frozen out by means of liquid air indicates that if substances of the type of aldehydes and acids are also formed in the acetylene flame, then their quantities must be relatively negligibly small. From this it follows that the main substances condensing in the trap at the temperature of liquid air and at a pressure not exceeding ten millimeters of mercury must be carbon dioxide and water, and also unconsumed acetylene. A rough approximate analysis of the condensate for these substances was conducted in the following manner. After freezing them out in the course of a certain time t the combustion ceased, was pumped free of uncondensed gas; the liquid air was removed, after which the condensed substances evaporated into a certain constant volume (equal to 6025 cm2). The pressure of these substances was measured with the aid of a U-shaped manometer filled with paraffin oil at every five seconds, and a curve was constructed of the increase in pressure, measured this way, with time. presence of three plateaus in the curve of such a type indicate that three gases enter into the condensate composition. First there evaporates acetylene, obviously, (in the course of the first 1-1.5 minutes after the removal of the liquid air); in the course of the next 1-2 minutes carbon dioxide evaporates and finally, after a prolonged delay of several minutes -- water. The height of the three plateaus yields in this way, PC2H2, PC

we find the partial pressures of C2H2, CO2 and H2O in the volume V (p,). From the values of p, found in this way it is not difficult to find the volumes v, according to the formula vi 760t

that is, the volumes of carbon dioxide (v_{CO}) and of water vapor (v_{H_2O}) forming in one second, 2 and the volume per second of acetylene ($v_{C_2H_2O}$) entering from the reaction vessel, all brought to 2^{H_2O} normal pressure.

Considering, further, that along with CO, and H₂O, there are formed in measurable quantities also in the flame carbon monoxide and hydrogen, and designating their quantities of volume as v_{CO} and v_H, from the formula

vc2H2 vc2H2 + xxc05 + xx = xc2H5 + xH50 + xH5,

which arises from the carbon and hydrogen balances in the mixture, we find the volumes v_{CO} and $v_{H_{\mathcal{O}}}$:

$$A^{H^{5}} = A^{C^{5}H^{5}}_{O} - A^{C^{5}H^{5}}_{O} + A^{H^{5}C}$$
;
 $A^{CO} = S(A^{C^{5}H^{5}}_{O} - A^{C^{5}H^{5}}_{O}) - A^{CO^{5}},$

here v_{C}^{O} is the continually measured volume of acetylene $^{O}2^{H}2$ which enters each second from the gasometer into the reaction vessel.

We display the results of two such analyses in table 2.

The volumes here are given in cubic centimeters per second. In the following columns of the table the percentage of consumption of acetylene are displayed, calculated according to the formula

As is seen from this table, under the conditions of our experiment the volume obtained of the carbon monoxide exceeds by 2-3 times the volume of carbon dioxide, which indicates a considerable concentration of CO in the flame. From the table, further, it follows that if the main products of the combustion of acetylene are, in terms of carbon, carbon monoxide, then in terms of hydrogen the main product is water, which undoubtedly it is necessary to ascribe to the greater ease of oxidation of H in comparison with CO. For this reason the

concentration of hydrogen in the flame (under the condi- | tions of the experiments under consideration) must be relatively small.

CONCLUSION

The method of the thermoelectric probe is applied to the study of rarified acetylene-air flames, burning at pressures up to ten mm Hg and at temperatures near 1000 K, and at various mixture compositions. There are presented considerations which permit the observed additional initial heating of the thermocouple costed with ZnO·CroOz to be ascribed to the catalytic recombination of atomic hydrogen. The determined concentration of the atomic hydrogen thusly established in the flame is of an order of magnitude which coincides with that calculated from the known concentration of hydroxyl. In absolute value, at a pressure of 10 mm Hg and at a temperature of 10000 K, the partial pressure of atomic hydrogen in the center of the combustion zone is of the order of a hundredth of a millimeter.

> Academy of Sciences USSR Institute of Chemical Physics Moscow

Received 6 January 1947

LITERATURE

- H. Kondratjewa and V. Kondratjew, Acta physiochimica URSS, 21, 4 (1946).
- I. Avramenko, Acta physiochimica URSS, 18, 58, 2. (1943).
- Ye. Kondrat'eva and V. Kondrat'ev, Zhurn. Fiz. 3. Khim. (Journal of Physical Chemistry), 20, 1239.
- V. Kondrat'ev, Spectroscopic Study of Chemical Reactions in the Gaseous State, Moscow - Leningrad, 1944.
- V. Kondrat'ev, Zhurn. Fiz. Khim., 20, 345 (1946).
 V. V. Voevodskiy, Dissertation, I Kh F (Institut Fizicheskoy Khimii Institute of Physical Chemistry), 1944.

-END-

FOR REASONS OF SPEED AND ECONOMY
THIS REPORT HAS BEEN REPRODUCED
ELECTRONICALLY DIRECTLY FROM OUR
CONTRACTOR'S TYPESCRIPT

THIS PUBLICATION WAS PREPARED UNDER CONTRACT TO THE UNITED STATES JOINT PUBLICATIONS RESEARCH SERVICE A FEDERAL GOVERNMENT ORGANIZATION ESTABLISHED TO SERVICE THE TRANSLATION AND RESEARCH NEEDS OF THE VARIOUS GOVERNMENT DEPARTMENTS